

Foreword

MARTIN KAUPP, VLADIMIR G. MALKIN

Magnetic resonance spectroscopy is an indispensable tool in many areas of the natural sciences, ranging from biology and medicine to materials research. In chemistry, nuclear magnetic resonance (NMR) spectroscopy and electron paramagnetic resonance (EPR) spectroscopy together arguably represent the most widely used class of spectroscopic techniques. It is thus understandable that the quantum-chemical treatment of magnetic resonance parameters has become an important branch of theoretical and computational chemistry. However, the history of quantitative calculations in this area from first principles is not as long as one might think. There are a number of difficulties with magnetic (vector) properties that prevented early success of quantum-chemical techniques. An example is the well-known gauge origin problem (e.g., for NMR chemical shifts). The practical solutions using distributed-gauge methods like IGLO and GIAO only started to bear fruit in applications in the mid-1980s. At last, chemical shifts could be computed with reasonable accuracy for systems of chemically relevant sizes! The progress marked by these seminal achievements was documented in the very successful conference on NMR chemical shifts at the University of Maryland in 1992, organized by Prof. J. A. Tossell.

Since then, the field has been transformed tremendously and may now be considered a mature and substantial subdiscipline of quantum chemistry. Progress has been made on various fronts: sophisticated post-Hartree–Fock methods have been developed to account for the effects of electron correlation. Density functional methods (DFT) came into play as a more economical alternative to include correlation in an approximate manner, applicable to calculations on large

molecules. This also opened the way to systems containing transition metals and other heavy elements. As a consequence, relativistic effects had to be treated, and considerable progress with the inclusion of both spin-free relativistic and spin-orbit effects has been made in the past few years and is continuing at present. The conceptually new insights that have developed are changing the qualitative interpretation of NMR chemical shifts (and of other NMR and EPR parameters). As the accuracy of the computed chemical shifts increases, additional factors, such as rovibrational and environmental effects, are being dealt with; both these areas are blossoming. The same is true for the combination of magnetic resonance parameter calculations with molecular dynamics simulations, which is being used increasingly to obtain dynamical information.

Until recently, chemical shift calculations dominated the focus of research and continue to be investigated extensively. Among the other NMR parameters, indirect spin–spin coupling constants are particularly difficult to compute, in part due to the need for an accurate treatment of electron correlation even with light main group systems. Again, the development of post-Hartree–Fock methods and the use of DFT expanded the limits of what might be done, and the calculations of spin–spin coupling constants can be expected to become routine during the next decade. Relativistic corrections also are being considered increasingly, and all the other aspects just mentioned for chemical shifts have been addressed at least preliminarily in recent work.

In 1997, in response to the need for a better exchange between workers in the field, plans for an international conference on the calculations of

magnetic properties of molecules took shape. It was clear that the "smaller brother" of NMR, EPR spectroscopy, also should be included. EPR hyperfine coupling constants are similar to NMR spin-spin coupling constants, both formally and in terms of computational difficulties. Electronic g-tensors of EPR are related conceptually to NMR chemical shift tensors (and on a different level also to spin-orbit corrections to NMR parameters). Hence, the symposium held on September 14–18, 1998 at the beautiful Smolenice Castle near Bratislava, Slovak Republic, was titled "International Conference on Quantum Chemical Calculations of NMR and EPR Parameters." More than 70 scientists from all over the world attended the meeting. The topics ranged widely from method development and validation to applications in many areas of chemistry, biology, and materials research. A number of lectures by experimental workers, including the plenary lecture of Nobel Laureate Richard R. Ernst (Zürich, Switzerland),

underscored the prominent role that quantum-chemical calculations now can play in various areas of magnetic resonance spectroscopy. Many stimulating discussions across subdiscipline borders took place in the pleasant surroundings of the castle. Ideas were exchanged between method developers and applications experts, between theoreticians and experimental workers, between specialists in NMR and EPR, and between younger and older researchers.

This special issue has grown out of the 1998 Smolenice Conference, but is not a symposium proceedings summary in the traditional sense. We have not required the contents of the manuscripts to be identical to those presented at the meeting. Moreover, the 11 articles published in this special JCC issue are not fully representative of the 4-day conference which consisted of more than 30 lectures and a similar number of posters. Thus, while several of the most important topics are included here (e.g., relativistic and environmental effects on



On the occasion of the NMR EPR-98 conference, Werner Kutzelnigg received the Diony'z Ilkovič Medal of the Slovak Academy of Sciences. From right to left: Drs. Werner Kutzelnigg (Bochum), Richard R. Ernst (Zürich), Vladimir G. Malkin (Bratislava), Olga L. Malkina (Bratislava), Martin Kaupp (Stuttgart), Ludger Buerstedde (German ambassador to the Slovak Republic), and Stefan Luby (President of the Slovak Academy of Sciences). Further photographs from and information on the program of the conference may be found at: <http://www.theochem.uni-stuttgart.de/~mkaupp/smolen.html>.

NMR and EPR parameters, the calculation and interpretation of chemical shifts, spin–spin coupling constants, and hyperfine coupling constants), other topics are not presented. A prime example is electronic g-tensors, the quantitative calculation of which has made much progress; several talks by most of the leading researchers in the field prompted considerable discussion throughout the conference.

Nevertheless, we hope that this issue will give the reader at least an impression of the remarkable progress that has been made in quantum-chemical computations of magnetic resonance parameters during the last few years. We expect developments to continue in this exciting and important area and look forward to the follow-up conference, which has been tentatively planned for 2001 or 2002 in Sweden.